

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2002-117854

(43)Date of publication of application : 19.04.2002

(51)Int.Cl.

H01M 4/60
C08F 8/00
C08F 12/14
C08F 20/10
C08F 38/00
C08G 75/02
H01M 4/02
H01M 4/04
H01M 4/62
H01M 10/40

(21)Application number : 2000-308520

(71)Applicant : NEC CORP

(22)Date of filing : 06.10.2000

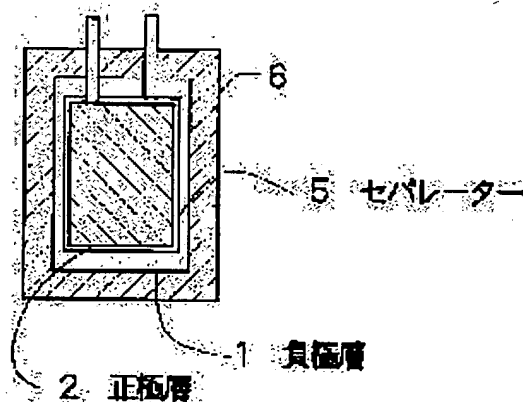
(72)Inventor : SATO MASAHARU
NAKAHARA KENTARO
MORIOKA YUKIKO
SAKAUCHI YUTAKA
IWASA SHIGEYUKI

(54) SECONDARY BATTERY AND ITS MANUFACTURING METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a new secondary battery which has high energy density, large capacity, and excellent stability.

SOLUTION: In the secondary battery using oxidation-reduction reaction of the active material in the charging/discharging process, the secondary battery containing the organic compound which is processed by ozone, is manufactured by the manufacturing method including a process in which the organic compound is made into an active material by the ozone processing, as the active material for both or either a positive electrode or a negative electrode. Thus, the secondary battery, which can perform charging/discharging of electricity with high energy density, and has excellent stability and safety with large capacity, and its simple manufacture, can be attained.



LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the

(19)日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11)特許出願公開番号

特開2002-117854

(P2002-117854A)

(43)公開日 平成14年4月19日 (2002.4.19)

(51)Int.Cl. ⁷	識別記号	F I	7-73-1 ⁸ (参考)
H 0 1 M 4/60		H 0 1 M 4/60	4 J 0 3 0
C 0 8 F 8/00		C 0 8 F 8/00	4 J 1 0 0
	12/14		5 H 0 2 9
	20/10		5 H 0 5 0
	38/00		

審査請求 未請求 請求項の数11 OL (全 11 頁) 最終頁に続く

(21)出願番号 特願2000-308520(P2000-308520)

(22)出願日 平成12年10月6日 (2000.10.6)

(71)出願人 000004237

日本電気株式会社

東京都港区芝五丁目7番1号

(72)発明者 佐藤 正春

東京都港区芝五丁目7番1号 日本電気株式会社内

(72)発明者 中原 謙太郎

東京都港区芝五丁目7番1号 日本電気株式会社内

(74)代理人 100086759

弁理士 渡辺 春平

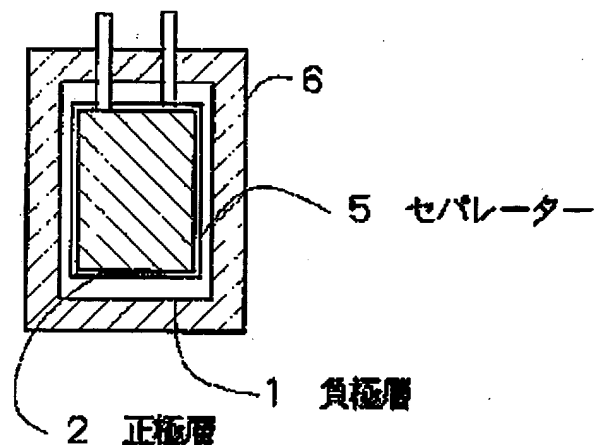
最終頁に続く

(54)【発明の名称】 二次電池およびその製造方法

(57)【要約】

【課題】 エネルギー密度が高く、大容量で安定性に優れた新規な二次電池を提供する。

【解決手段】 活物質の酸化還元反応を充放電過程に利用する二次電池において、正極および負極あるいはいずれか一方の電極の活物質として、オゾン処理した有機化合物を含有する二次電池を、オゾン処理による有機化合物の活物質化工程を含む製造方法で製造することにより、充放電を高エネルギー密度で行うことが可能な、大容量で安定性、安全性に優れた二次電池、およびその簡便なる製造が可能となる。



* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the rechargeable battery which uses the oxidation reduction reaction of an active material for a charge-and-discharge process, and its manufacture approach. More, it is the rechargeable battery which uses the oxidation reduction reaction of an active material for a charge-and-discharge process at a detail, and while the organic compound ozonized as main active materials is included, energy density is large and it is related with the rechargeable battery excellent in stability and safety, and its manufacture approach.

[0002]

[Description of the Prior Art] The demand on a small mass cell with the big energy density used for these is increasing with a rapid commercial-scene expansion of a notebook sized personal computer, a cellular phone, etc. And in order to meet this demand, the rechargeable battery which used the electrochemical reaction accompanying that charge transfer by making alkali-metal ion, such as a lithium ion, into electric charge support is developed. Especially, the rechargeable lithium-ion battery is used for various electronic equipment as a mass cell with the big energy density excellent in stability. In such a rechargeable lithium-ion battery, as an active material, lithium content transition-metals oxide is used for a positive electrode, carbon is used for the negative electrode, and charge and discharge are performed using the insertion reaction and elimination reaction of a lithium ion to these active materials, for example.

[0003] However, since the transition-metals oxide with large specific gravity as an active material of a positive electrode was used for this rechargeable lithium-ion battery, it had the problem that the cell capacity per unit mass was not enough.

[0004] Then, the attempt which is going to develop a mass cell using a more nearly lightweight electrode material has been examined. For example, the cell which used for the active material of a positive electrode the organic compound which has a disulfide bond is indicated by the U.S. Pat. No. 4,833,048 official report and the patent No. 2715778 official report. This uses the electrochemical oxidation reduction reaction of an organic compound based on generation and dissociation of a disulfide bond as a principle of a cell. However, this cell had the problem that the recombination effectiveness of the dissociated disulfide bond was small, and the stability in a charge condition or a discharge condition was inadequate, although fixed effectiveness was acquired in the point of constitute the mass cell of a high energy consistency, since the organic compound which uses an element with small specific gravity, such as sulfur and carbon, as a principal component was used as an electrode material.

[0005] Moreover, the cell which used the conductive polymer for the electrode material is proposed as a cell which similarly used the organic compound for the active material. This is the cell which made the principle the dope reaction and dedope reaction of electrolyte ion to a conductive polymer. In addition, it is defined as the reaction which stabilizes excitons produced by electrochemical oxidation reaction or reduction reaction of a conductive polymer, such as an electric charge soliton and polaron, with a counter ion with the dope reaction described here, and, on the other hand, is defined as the reverse reaction of a dope reaction, i.e., the reaction which oxidizes or returns electrochemically the exciton stabilized with the counter ion, with a dedope reaction.

[0006] The cell which uses such a conductive polymer as the active material of a positive electrode or a negative electrode is indicated by the U.S. Pat. No. 4,442,187 official report. Since this cell used for the electrode material the organic compound which consists only of an element with small specific gravity, such as carbon and nitrogen, development was expected as a mass cell. However, since the exciton produced by the electrochemical oxidation reduction reaction continues and delocalized in the large range of pi electron conjugated system, there was a property in which they interact in a conductive polymer and a limitation was generated also to the concentration of the exciton to generate, there was a problem that the capacity of a cell was restricted. Therefore, although fixed effectiveness was acquired in respect of lightweight-izing of a cell by the cell which uses such a conductive polymer as an electrode material, in the point of large-capacity-izing of a cell, it was still inadequate.

[0007] On the other hand, the ozonization technique is developed as one of the surface treatment approaches of various ingredients. Generally, by contact in ozone gas, or the UV irradiation under an oxygen ambient atmosphere, this technique

tends to improve the wettability and the adhesive property on the front face of a base material, and is industrially carried out in various fields.

[0008] The attempt for which the field of a rechargeable battery also tends to improve the repeat life and stability of a cell by using such ozonization is performed. For example, the method of manufacturing the mass positive-electrode ingredient which does not have a lithium deficit a pyrolysis or by calcinating under an ozone ambient atmosphere in a nickel compound and a lithium compound is indicated by JP,11-16572,A and JP,11-176439,A.

[0009] Moreover, the rechargeable battery with little capacity degradation accompanying a cycle which uses the ozonized manganic acid ghost as a positive-electrode ingredient is indicated by JP,11-25970,A. Furthermore, the cell which can shorten an aging process is indicated by using for JP,11-389852,A the separator which carried out ultraviolet treatment. However, by these ozonization, in that the stability of a cell etc. is improved, although fixed effectiveness was acquired, effectiveness sufficient in respect of large-capacity-izing of a cell was not acquired.

[0010] Although the cell of various classes is proposed in order to realize a mass cell as stated above, about the approach of manufacturing the cell which whose energy density was high and was excellent in stability with large capacity, and such a cell simple, it is not yet established.

[0011]

[Problem(s) to be Solved by the Invention] As mentioned above, manufacture of the mass cell which exceeds the present condition in the lithium ion battery using transition-metals oxide as an active material of a positive electrode since the specific gravity of an element is large was theoretically difficult. Moreover, although the method of ozonizing an electrode and an active material was also performed, sufficient effectiveness was not acquired from a viewpoint of large-capacity-izing of a cell. Then, as a result of this invention persons' inquiring wholeheartedly, it was inactive electrochemically, and by ozonizing the organic compound which was not able to be used as an electrode active material until now, it became possible to perform an electrochemical oxidation reduction reaction, and found out that it could use as an active material of a cell. Therefore, this invention aims at offering the manufacture approach acquired energy density is high and simple [the rechargeable battery which was excellent in stability with large capacity, and such a rechargeable battery], and efficiently by using such a specific organic compound as an active material of an electrode.

[0012]

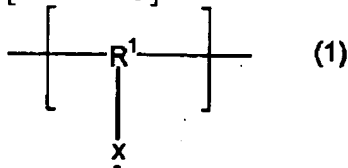
[Means for Solving the Problem] In order to attain said purpose, according to this invention, the rechargeable battery containing the organic compound which ozonized the oxidation reduction reaction of an active material in the rechargeable battery used for a charge-and-discharge process as an active material of a positive electrode and a negative electrode, or one of electrodes is offered. Thus, while being able to use easily the organic compound processed by the ozone which is a strong oxidizing gas by constituting as an active material, energy density is high and the rechargeable battery which was excellent in stability with large capacity can be obtained easily.

[0013] In addition, generally, ozone is gas which has strong oxidizing power, and since it excels also in reactivity with an organic compound, it is used for many years as the approach of the surface treatment aiming at the improvement in wettability of plastics, or *****. Moreover, according to old research, it has become clear, for example by ozonizing plastics etc. that functional groups, such as a hydroxyl group (- OH radical) which is a polar functional group, a carbonyl group (-C(=O)-radical), and a carboxyl group (-COOH radical), are formed on the front face.

[0014] Moreover, in constituting this invention, it is desirable that it is the giant-molecule radical compound with which the ozonized organic compound includes the structural unit expressed with the following general formula (1) and a general formula (2), or one of general formulas.

[0015]

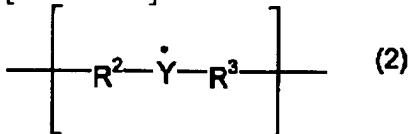
[Formula 3]



[0016] [-- among a general formula (1), a substituent R1 is a permutation or an unsubstituted alkylene group, an alkenylene group, or an arylene radical, and X is an oxy-radical radical, a nitroxyl radical radical, a sulfur radical radical, a HIDORAJIRU radical radical, a carbon radical radical, or a boron radical radical.]

[0017]

[Formula 4]



[0018] [-- R2 and R3 are independent of mutual among a general formula (2), it is a permutation or an unsubstituted alkylene group, an alkenylene group, or an arylene radical, and Y is a nitroxyl radical radical, a sulfur radical radical, a HIDORAJIRU radical radical, or a carbon radical radical.]

[0019] Thus, since an oxidation reduction reaction advances only by the radical part in a giant-molecule radical compound by constituting, a cycle property can obtain easily the rechargeable battery excellent in the stability independent of diffusion of an active material. Moreover, with the giant-molecule radical compound which has such a structural unit, since the concentration of a reactive site can be increased as a result of the unpaired electron which reacts localizing and existing in a radical atom, a high energy consistency and a mass rechargeable battery can be obtained.

[0020] In addition, generally, although radicals are the chemical species which were rich in the reactivity which has an unpaired electron and there is much what has a certain amount of life and disappears by the interaction with the surrounding matter, there are some which serve as a stabilization radical kind depending on a mesomeric effect, steric hindrance, and the condition of a solvation. Moreover, diffusing the radical generated on the organic compound front face inside is also considered.

[0021] Moreover, in constituting the rechargeable battery of this invention, it is desirable that the ozonized organic compound is an aromatic compound. Thus, since an organic compound can be constituted only from elements, such as carbon with small mass, hydrogen, and oxygen, by constituting, a rechargeable battery with the big energy density per unit mass can be obtained easily.

[0022] Moreover, in constituting the rechargeable battery of this invention, it is desirable that the spin concentration in the electron-spin-resonance (it is hereafter written as ESR.) spectrum of the ozonized organic compound is more than 1020 spin / g. Thus, by constituting, energy density is high and the rechargeable battery which was excellent in stability with large capacity can be obtained easily. In addition, it is known that the above-mentioned stabilization radical kind generally has the spin concentration in an ESR spectrum within the limits of 1019 - 1023 spin / g over long duration.

[0023] Moreover, in constituting the rechargeable battery of this invention, it is desirable that this rechargeable battery is a rechargeable lithium-ion battery. Thus, by constituting, the mass rechargeable battery excellent in stability can be obtained.

[0024] In addition, although the ozonized organic compound is used as an active material of an electrode in this invention, the attempt which is going to improve the wettability etc. has already been performed as a conventional technique by ozonizing to active materials, such as a nickel compound and a carbon material, as above-mentioned. Therefore, although possibility that the organic compound ozonized as a result will generate is also considered when an organic compound is used for the binder which constitutes an active material layer for example, there are few organic compounds contained in the electrode layer of the conventional cell, and they are only number wt.% extent. That is, even if it is the case where it ozonizes to such an organic compound, the capacity and energy density of a cell which are obtained hardly change, but it is thought that characteristic effectiveness like this invention is not acquired.

[0025] On the other hand, since the rechargeable battery of this invention is using the ozonized organic compound as the main active materials, its energy density is high and it can obtain easily the rechargeable battery which was excellent in stability with large capacity. Moreover, although it will not be limited especially if the amount of the ozonized organic compound to the whole active material layer is an amount from which this ingredient can serve as the main active materials in this invention, generally it is carried out above 10wt(s).% from which large-capacity-izing and high energy consistency-ization become remarkable.

[0026] Moreover, another mode of this invention is the manufacture approach of a rechargeable battery of using the oxidation reduction reaction of an active material for a charge-and-discharge process, and is characterized by including the formation process of an electrode, and an aging process an active material chemically-modified [of the organic compound by ozonization] degree. By doing in this way, energy density is high and the rechargeable battery which was excellent in stability with large capacity can be manufactured easily.

[0027] Moreover, in enforcing the manufacture approach of the rechargeable battery of this invention, it is desirable to include the process which mixes a binder and a solvent to an organic compound, and produces a coating to the formation process of the above-mentioned electrode, and the process which applies the above-mentioned coating to a charge collector, and forms an organic compound layer on a charge collector. By doing in this way, energy density is high and the rechargeable battery which was excellent in stability with large capacity can be manufactured easily.

[0028] Moreover, in enforcing the manufacture approach of the rechargeable battery of this invention, it is desirable to carry out as a back process of the process which forms the last process or the above-mentioned organic compound layer of a process which creates the above-mentioned coating for an active material chemically-modified [above-mentioned] degree. By doing in this way, energy density is high and the rechargeable battery which was excellent in stability with large capacity can be manufactured easily.

[0029] Moreover, in enforcing the manufacture approach of the rechargeable battery of this invention, it is desirable to irradiate ultraviolet rays to ozonization under an ozone gas ambient atmosphere or an oxygen ambient atmosphere. By doing in this way, an organic compound can be ozonized efficiently.

[0030] Moreover, in enforcing the manufacture approach of the rechargeable battery of this invention, it is desirable to irradiate the above-mentioned ultraviolet rays using a low-pressure mercury lamp or an excimer UV lamp. While ultraviolet treatment is certainly performed by doing in this way, an organic compound can be ozonized efficiently.

[0031]

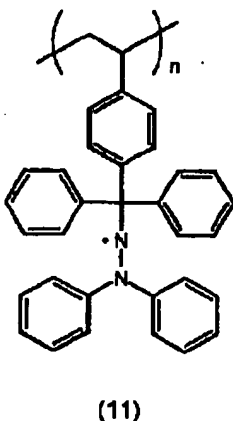
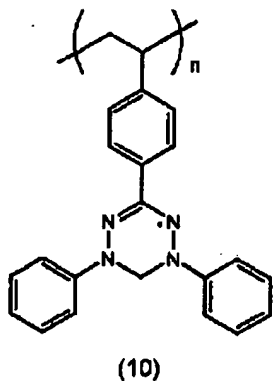
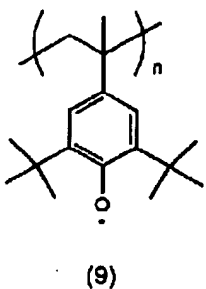
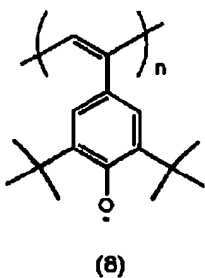
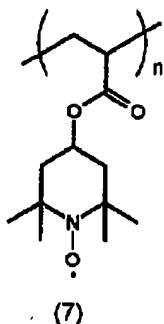
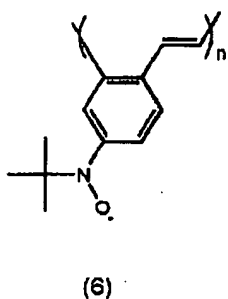
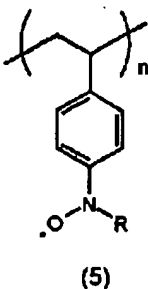
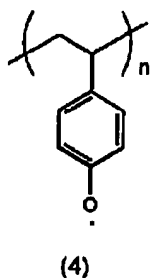
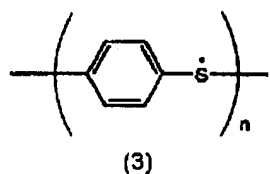
[Embodiment of the Invention] The operation gestalt of the rechargeable battery of [rechargeable battery] this invention has the configuration which piled up the negative-electrode layer 1 and the positive-electrode layer 2 through the separator 5 containing an electrolyte, as shown in drawing 1 . In this invention, the active material used for the negative-electrode layer 1 or the positive-electrode layer 2 is the ozonized organic compound. Moreover, although the sectional view of a laminating mold cell is shown in drawing 2 , the structure has the structure which piled up the negative-electrode charge collector 3, the negative-electrode layer 1, the separator 5 containing an electrolyte, the positive-electrode layer 2, and the positive-electrode charge collector 4 in order. In this invention, especially the laminating approach of a positive-electrode layer and a negative-electrode layer is not limited, but can use what carried out the multilayer laminating, the thing which combined with both sides of a charge collector what carried out the laminating, the wound thing.

[0032] (1) Although an organic compound is used in active material ** ingredient 1 this invention as an ingredient which ozonizes, this is because it can be used as an active material in which an electrochemical oxidation reduction reaction is possible by ozonizing an organic compound by making a radical generate on the front face of an organic compound, and using the radical. Therefore, although especially the class of organic compound which ozonizes is not restricted, it is desirable that the electrochemical oxidation reduction reaction after ozonization is the organic compound which can be used for the charge-and-discharge process of a cell.

[0033] Moreover, since the ozonized organic compound is excellent in the workability in the case of forming an electrode active material layer, it is desirable that it is a giant-molecule radical compound including the structural unit expressed with a general formula (1) and a general formula (2), or one of general formulas. As such a giant-molecule radical compound, the compound expressed with following general formula (3) - (11) can be mentioned.

[0034]

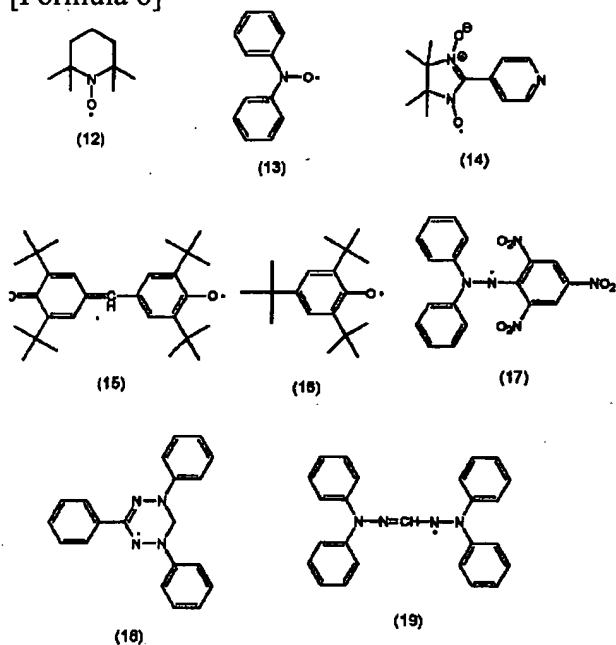
[Formula 5]



[0035] Moreover, it is desirable that they are a low-molecular radical compound which is expressed with following formula (12) - (19) besides the above-mentioned giant-molecule radical compound, and a partial saturation radical compound from the point of the capacity manifestation after ozonization as an ozonized organic compound. In addition, a kind independent or two sorts or more can be mixed and used for these radical compounds.

[0036]

[Formula 6]



[0037] In this invention, an organic compound is the generic name of all the carbon compounds except a small number of. However, the effectiveness acquired by ozonization in the polycrystalline substance with which the crystals which consist of only carbon atoms represented by the crystal which developed only from the carbon atom represented by graphite, a diamond, fullerene, etc., soft carbon, hard carbon, etc. gathered is small. With these compounds, this reason is considered because that effectiveness will be limited only on a solid front face, as a result of controlling diffusion of the radical inside [subsequent] bulk, although a radical is formed on that front face of ozonization. On the other hand, in common organic compounds other than the above-mentioned compound, the radical generated on the front face can be spread easily, and that also including a molecular crystal can be effectively used for the interior of bulk as an active material.

[0038] ** Although the ozonized organic compound can be used in ingredient 2 this invention as an active material of a positive electrode and a negative electrode, or one of electrodes as above-mentioned, it is desirable to use the organic compound ozonized especially as an active material of a positive electrode from a viewpoint of energy density.

[0039] In addition, when using these organic compounds as an active material of one of the electrodes of a positive electrode and cathode, the next ingredient can be used as an active material of other electrodes. That is, when using the organic compound ozonized as an active material of a negative-electrode layer, a metallic-oxide particle, a disulfide compound, a conductive polymer, etc. are used as an active material of a positive-electrode layer. The manganic acid lithium which has a manganic acid lithium or Spinel structure, such as LiMnO_2 and $\text{Li}_x\text{Mn}_2\text{O}_4$ ($0 < x < 2$), as a metallic oxide here, for example, MnO_2 , LiCoO_2 , LiNiO_2 , or $\text{Li}_x\text{V}_2\text{O}_5$ ($0 < x < 2$) as a disulfide compound A dithio glycol, 2,5-dimercapto-1,3,4-thiadiazole, S-triazine-2,4,6-trithiol, etc. are mentioned for polyacetylene, polyphenylene, the poly aniline, polypyrrole, etc. as a conductive polymer again, respectively. In this invention, these positive-electrode layer ingredients can be used combining a kind independent or two sorts or more.

[0040] On the other hand, when using the organic compound ozonized as an active material of a positive-electrode layer, kind independent, such as a graphite, amorphous carbon, and lithium metal, a lithium alloy, lithium ion occlusion carbon, and a conductive polymer, or two or more sorts of combination are used as an active material of a negative-electrode layer. It is not limited especially as these configurations, for example, a bulk-like thing and powder can be used for a briquette, a fibrous thing, a flake-like thing, etc. with a lithium metal in addition to a thin film-like thing. Furthermore, the organic compound which ozonized with the well-known active material and was obtained conventionally may be mixed, and you may use as a compound active material.

[0041] (2) In auxiliary electric conduction material and ionic conduction nominal member this invention, in case the electrode layer containing the ozonized organic compound is formed, auxiliary electric conduction material and an ionic conduction nominal member can also be mixed in order to reduce an impedance. As these ingredients, as auxiliary electric conduction material, conductive polymers, such as carbonaceous particles, such as graphite, carbon black, and acetylene

black, the poly aniline, polypyrrole, the poly thiophene, polyacethylene, and the poly acene, are mentioned, and a polymer gel electrolyte, a solid polymer electrolyte, etc. are mentioned as an ionic conduction nominal member, respectively.

[0042] (3) In binder this invention, in order to strengthen the connection between each component, a binder can also be used. As such a binder, resin binders, such as polyvinylidene fluoride, a vinylidene fluoride-hexafluoropropylene copolymer, a vinylidene fluoride-tetrafluoroethylene copolymer, styrene butadiene rubber, polypropylene, polyethylene, polyimide, and various polyurethane, are mentioned.

[0043] (4) In catalyst this invention, in order to carry out electrode reaction to lubrication more, the catalyst which promotes an oxidation reduction reaction can also be used. As such a catalyst, basic compounds, such as conductive polymers, such as the poly aniline, polypyrrole, the poly thiophene, polyacethylene, and the poly acene, a pyridine derivative, a pyrrolidone derivative, a benzimidazole derivative, a benzothiazole derivative, and an acridine derivative, a metal ion complex, etc. are mentioned.

[0044] (5) In charge collector this invention, metallic foils, such as nickel, aluminum, copper, gold, silver, an aluminium alloy, and stainless steel, a metal plate, a mesh-like electrode, a carbon electrode, etc. can be used as the negative-electrode charge collector 3 and a positive-electrode charge collector 4. Moreover, the catalyst effectiveness may be given to such a charge collector, or the chemical bond of an active material and the charge collector may be carried out. It is also desirable to use the separator which consists of a porosity film on the other hand so that the above-mentioned positive electrode and a negative electrode may not contact, and a nonwoven fabric.

[0045] (6) In electrolyte this invention, an electrolyte 5 performs electric charge mediated transport between the two poles of the negative-electrode layer 1 and the positive-electrode layer 2, and, generally has the ion conductivity of 10^{-5} - 10^{-1} S/cm at the room temperature. In this invention, the electrolytic solution which dissolved for example, the electrolyte salt in the solvent can be used as an electrolyte. As such an electrolyte salt, an ingredient with conventionally well-known LiPF_6 , LiClO_4 , LiBF_4 , LiCF_3SO_3 , $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$, $\text{Li}(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}$, $\text{Li}(\text{CF}_3\text{SO}_2)_3\text{C}$, $\text{Li}(\text{C}_2\text{F}_5\text{SO}_2)_3\text{C}$, etc. can be used, for example. Moreover, as a solvent of an electrolyte salt, organic solvents, such as ethylene carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate, methylethyl carbonate, gamma-butyrolactone, a tetrahydrofuran, dioxolane, a sulfolane, dimethylformamide, dimethylacetamide, and a N-methyl-2-pyrrolidone, can be used, for example. In addition, in this invention, these solvents can also be used as a kind independent or two or more sorts of partially aromatic solvents.

[0046] Furthermore, in this invention, a solid electrolyte can also be used as an electrolyte. As a high molecular compound used for such a solid electrolyte A polyvinylidene fluoride and vinylidene fluoride-hexafluoropropylene copolymer, A vinylidene fluoride-ethylene copolymer, a vinylidene fluoride-mono-fluoro ethylene copolymer, A vinylidene fluoride-trifluoro ethylene copolymer, a vinylidene fluoride-tetrafluoroethylene copolymer, Vinylidene fluoride system polymers, such as a vinylidene fluoride-hexafluoropropylene-tetrafluoroethylene ternary polymerization object, An acrylonitrile-methyl methacrylate copolymer, an acrylonitrile-methyl acrylate copolymer, An acrylonitrile-ethyl methacrylate copolymer, an acrylonitrile-ethyl acrylate copolymer, An acrylonitrile-methacrylic-acid copolymer, an acrylonitrile-acrylic-acid copolymer, Polyethylene oxide and ethyleneoxide-propylene oxide copolymers, these acrylate objects, the polymer of a methacrylate object, etc. are mentioned to acrylic nitril system polymers, such as an acrylonitrile-vinyl acetate copolymer, and a pan. In addition, a solid electrolyte may be used as it is only with a high molecular compound, using what was made to contain the electrolytic solution in these high molecular compounds, and was made into gel.

[0047] (7) Also about a configuration and the configuration of a rechargeable battery, especially as long as it is the organic compound which the active material ozonized, it is not limited, but it can apply to the configuration of a cylindrical cell, a coin mold cell, a square shape cell, a film mold cell, a carbon button mold cell, etc.

[0048] The operation gestalt of the manufacture approach of [manufacture approach] this invention is the manufacture approach of a rechargeable battery of using the oxidation reduction reaction of an active material for a charge-and-discharge process, and includes the formation process of an electrode, and an aging process an active material chemically-modified [of the organic compound by ozonization] degree.

[0049] In this invention, ozonization is the approach of processing an organic compound using ozone gas. As such an approach, the approach of holding an organic compound in the ambient atmosphere containing ozone gas, the method of irradiating ultraviolet rays under an oxygen ambient atmosphere, making ozone gas generate from an oxygen atom, and processing an organic compound, etc. are mentioned, for example. In addition, generally, if ultraviolet rays are irradiated at an oxygen molecule, an oxygen molecule absorbs 185nm light, and generates ozone, and it is known that this ozone will generate active oxygen with 254nm light.

[0050] Although ultraviolet rays can be generated using ultraviolet ray lamps, such as a hydrogen discharge tube, a xenon lamp, a low-pressure mercury lamp, and an excimer UV lamp, in this invention, it is desirable to use a low-pressure mercury lamp and an excimer UV lamp especially from excelling in the effectiveness of ozonization. Among these, as a low-pressure mercury lamp, a straight pipe mold lamp like SUVby Sen Lights Corp.110D etc. is used, for example. Moreover, as an excimer UV lamp, a coherent excimer laser, an incoherent dielectric barrier discharge excimer lamp, etc.

are used. As such an excimer laser, a fluoride argon laser, krypton fluoride laser, etc. are mentioned, and a xenon excimer lamp, a chlorination krypton excimer lamp, etc. are mentioned as a dielectric barrier discharge excimer lamp. Moreover, by this manufacture approach, ultraviolet rays can also be irradiated under an ozone gas ambient atmosphere.

[0051] By this manufacture approach, it is not restricted especially about the stage to ozonize to an organic compound. For example, although the process which mixes a binder and a solvent to an organic compound, and produces a coating as a formation process of an electrode, the process which applies this coating to a charge collector and forms an organic compound layer on a charge collector are included when manufacturing the rechargeable battery of this invention as cylindrical or a square shape cell. In this case, an active material chemically-modified [of the organic compound by ozonization] degree may be performed after the process which may carry out before the process which produces the above-mentioned coating, and forms the above-mentioned organic compound layer. Moreover, in this invention, the temperature which ozonizes, time amount, especially an ozone level, etc. are not limited, but they are chosen suitably, looking at the effectiveness of processing.

[0052] Moreover, in this invention, the radical compound generated by ozonization is stabilized by performing aging actuation accompanied by charge or discharge. Therefore, it can be determined by whether the reaction (chlorination) of a radical compound and cations, such as a lithium, is performed in process of any of the charge and discharge of a cell whether to perform aging actuation in the discharge process after cell formation or carry out in a charge process. In addition, by such aging actuation, the device in which the radical compound generated by ozonization spreads and goes to the interior of a solid-state by reacting with cations, such as a lithium, is considered. Moreover, although especially the conditions of the aging actuation in this invention are not limited, it is desirable to carry out from the point that the effectiveness is demonstrated effectively, above a room temperature, and it is more desirable to carry out in the state of heating of 40 degrees C or more.

[0053]

[Example] Hereafter, although an example explains the detail of this invention concretely, this invention is not limited to these examples.

(Example 1)

(1) The production polyphenylene sulfide powder (particle size of 10 micrometers) of a rechargeable lithium-ion battery was opened to homogeneity on the glass plate, and it processed by holding for 6 hours with the air which contains the ozone of 5 volume % in a glass container. When a part of this powder was taken out picking and the ESR spectrum was measured, that spin concentration was increasing from below the 1017 spin / g before ozonization to 2×10^{20} spin / g. From this, it was checked that the radical has occurred in a polyphenylene sulfide particle.

[0054] Next, 50g N-methyl pyrrolidone was made to distribute 1g of ozonized polyphenylene sulfide powder, and the black slurry was obtained, when it mixed until it added 60mg of graphite powder further as auxiliary electric conduction material to this and the whole became homogeneity. This slurry 2g was dropped at the front face of the aluminium foil (area: 1.5cmx1.5cm, thickness:100micrometer) equipped with lead wire, and after developing so that the whole may serve as uniform thickness with a wire bar, when carrying out reduced pressure drying at 120 degrees C for 6 hours, the electrode layer containing the polyphenylene sulfide particle which the solvent evaporated and was ozonized on aluminium foil was formed.

[0055] Next, 600mg of vinylidene fluoride-hexafluoropropylene copolymers was added to ethylene carbonate / 1,400mg (mixing ratio 1:1) of propylene carbonate mixed solutions which contained LiPF₆ of 1 mol/l as an electrolyte salt, tetrahydrofuran 11.3g was added further, and it stirred at the room temperature. After dissolving a vinylidene fluoride-hexafluoropropylene copolymer, applied the electrolytic solution on the glass plate which gave the level difference, and left it at the room temperature for 1 hour, the tetrahydrofuran was made to season naturally, and the cast film with a thickness of 1mm was obtained. This gel electrolyte film was cut down to 2.0cmx2.0cm, the laminating was carried out to the electrode layer containing the ozonized polyphenylene sulfide particle which was produced previously, and lithium lamination copper foil (30 micrometers of lithium thickness, 20 micrometers of thickness of copper foil) equipped with lead wire was piled up further. Then, the whole was inserted with the sheet made from polytetrafluoroethylene with a thickness of 5mm, the pressure was applied, and the rechargeable lithium-ion battery was produced.

[0056] (2) evaluation of a rechargeable lithium-ion battery -- when the rechargeable lithium-ion battery produced as mentioned above was connected to the charge and discharge test machine, open circuit voltage is 1.8V and discharge to 1.0V was immediately performed by the constant current which is 0.01mA. Then, the charge and discharge test was performed by 0.01mA constant current, having used a positive electrode and lithium lamination copper foil as the negative electrode for the electrode layer containing the polyphenylene sulfide particle which carried out aging processing for 6 hours, and subsequently ozonized this cell at 45 degrees C. Consequently, the electrical-potential-difference flat part was accepted in the 1.8V neighborhood, and operating as a cell was checked. Furthermore, when the charge and discharge of this cell were repeated and carried out, over ten or more cycles, charge and discharge are possible and operating as a rechargeable battery was checked.

[0057] (Example 2)

(1) The black slurry was obtained, when it mixed until it made 50g N-methyl pyrrolidone distribute 1g of the powder as it is, it added 60mg of graphite powder further as auxiliary electric conduction material to this using the polyphenylene sulfide of the production example 1 of a rechargeable lithium-ion battery and the whole became homogeneity. It was dropped at the front face of the aluminium foil which used this slurry 2g in the example 1, and when reduced pressure drying was developed and carried out by the same approach as an example 1, the electrode layer containing a polyphenylene sulfide particle was formed on aluminium foil.

[0058] Next, UV irradiation processing was performed in air using the black light equipped with the low-pressure mercury lamp (the Sen Lights Corp. make, SUV110D) for the obtained electrode layer. In addition, distance of a sample and the light source was set to 5cm, and performed processing at 30 degrees C for 2 hours. Although especially change was not seen as compared with UV irradiation before, when the appearance of the sample after ultraviolet treatment took out a part of sample after processing and measured the ESR spectrum, the spin concentration is more than 1020 spin / g, and it was checked that the radical has occurred in a polyphenylene sulfide particle.

[0059] The laminating of the gel electrolyte layer used for this electrode layer in the example 1 was carried out, the lithium lamination copper foil equipped with lead wire by the same approach as an example 1 was inserted with superposition and the sheet made from polytetrafluoroethylene, the pressure was applied, and the rechargeable lithium-ion battery was produced.

[0060] (2) evaluation of a rechargeable lithium-ion battery -- when the rechargeable lithium-ion battery produced as mentioned above was connected to the charge and discharge test machine, open circuit voltage is 1.8V and discharge to 1.0V was immediately performed by the constant current which is 0.01mA. Then, the charge and discharge test was performed by 0.01mA constant current, having used a positive electrode and lithium lamination copper foil as the negative electrode for the electrode layer containing the polyphenylene sulfide which carried out aging processing and subsequently carried out ultraviolet treatment of this cell at 45 degrees C. Consequently, the electrical-potential-difference flat part was accepted in the 1.8V neighborhood, and operating as a cell was checked. Furthermore, when the charge and discharge of this cell were repeated and carried out, over ten or more cycles, charge and discharge are possible and operating as a rechargeable battery was checked.

[0061] (Example 3)

(1) The electrode layer which considers as a black slurry, develops, dries by the same approach as an example 2 using the polyphenylene sulfide of the production example 1 of a rechargeable lithium-ion battery, and contains a polyphenylene sulfide particle on aluminium foil was formed.

[0062] Next, excimer UV irradiation processing was performed for the obtained electrode layer using the xenon excimer UV lamp (USHIO, INC. make). In addition, distance of a sample and the light source was set to 5cm, and performed processing for 10 minutes at 30 degrees C. Although especially change was not seen as compared with exposure before, when the appearance of the sample after excimer UV irradiation took out a part of sample after processing and measured the ESR spectrum, the spin concentration is more than 1020 spin / g, and it was checked that the radical has occurred in a polyphenylene sulfide particle.

[0063] The laminating of the gel electrolyte layer used for this electrode layer in the example 1 was carried out, the lithium lamination copper foil equipped with lead wire by the same approach as an example 1 was inserted with superposition and the sheet made from polytetrafluoroethylene, the pressure was applied, and the rechargeable lithium-ion battery was produced.

[0064] (2) evaluation of a rechargeable lithium-ion battery -- when the rechargeable lithium-ion battery produced as mentioned above was connected to the charge and discharge test machine, open circuit voltage is 1.8V and discharge to 1.0V was immediately performed by the constant current which is 0.01mA. Then, aging processing of this cell was carried out at 45 degrees C, and subsequently the charge and discharge test was performed by 0.01mA constant current, having used a positive electrode and lithium lamination copper foil as the negative electrode for the electrode layer containing the polyphenylene sulfide which carried out excimer UV irradiation processing. Consequently, the electrical-potential-difference flat part was accepted in the 1.8V neighborhood, and operating as a cell was checked. Furthermore, when the charge and discharge of this cell were repeated and carried out, over ten or more cycles, charge and discharge are possible and operating as a rechargeable battery was checked.

[0065] (Example 1 of a comparison) The electrode layer which considers as a black slurry, develops, dries by the same approach as an example 2 using the polyphenylene sulfide of an example 1, and contains a polyphenylene sulfide particle on aluminium foil was formed. Next, the laminating of the gel electrolyte layer used for the obtained electrode layer in the example 1 as it was was carried out, the lithium lamination copper foil equipped with lead wire by the same approach as an example 1 was inserted with superposition and the sheet made from polytetrafluoroethylene, the pressure was applied, and the rechargeable lithium-ion battery was produced. When the rechargeable lithium-ion battery produced as mentioned above was connected to the charge and discharge test machine, open circuit voltage was not accepted; and charge and discharge could not perform it, either, and the actuation as a cell was not checked.

[0066] (Example 4)

(1) It was ozonized by the same approach as in example 1 except replacing with the polyphenylene sulfide powder of the production example 1 of a rechargeable lithium-ion battery, and using PORIPA (poly(2,2,6,6-tetramethylpiperidin-1-yl)phenyl) phenol powder. When a part of this powder was taken out for picking and the ESR spectrum was measured, spin concentration was increasing from below the 1017 spin / g before processing to 1020 spin / g. From this, it was checked that the radical has occurred in a PORIPA (poly(2,2,6,6-tetramethylpiperidin-1-yl)phenyl) phenol particle.

[0067] Next, the 50g tetrahydrofuran was made to dissolve 1g of ozonized PORIPA (poly(2,2,6,6-tetramethylpiperidin-1-yl)phenyl) phenol powder, and the black slurry was obtained, when it mixed until it added 60mg of graphite powder further as auxiliary electric conduction material to this and the whole became homogeneous. This slurry was developed and dried by the same approach as in example 1, and the electrode layer included in the end of PORIPA (poly(2,2,6,6-tetramethylpiperidin-1-yl)phenyl) phenol powder it was ozonized on aluminium foil was formed.

[0068] Next, the laminating of the gel electrolyte layer used for this electrode layer in the example 1 was carried out, the lithium lamination copper foil equipped with lead wire by the same approach as in example 1 was inserted with superposition and the sheet made from polytetrafluoroethylene, the pressure was applied, and the lithium ion rechargeable battery was produced.

[0069] (2) evaluation of a rechargeable lithium-ion battery -- when the rechargeable lithium-ion battery produced as mentioned above was connected to the charge and discharge test machine, open circuit voltage is 1.5V and discharge to 1.0V was immediately performed by the constant current which is 0.01mA. Then, the charge and discharge test was performed by 0.01mA constant current, having used a positive electrode and lithium lamination copper foil as the negative electrode for the electrode layer containing the PORIPA (poly(2,2,6,6-tetramethylpiperidin-1-yl)phenyl) phenol which carried out aging processing and subsequently ozonized this cell at 45 degrees C. Consequently, the electrical-potential-difference flat part was accepted in the 1.8V neighborhood, and operating as a cell was checked. Furthermore, when the charge and discharge of this cell were repeated and carried out, over ten or more cycles, charge and discharge are possible and operating as a rechargeable battery was checked.

[0070] (Example 5)

(1) It was ozonized by the same approach as in example 1 except replacing with the polyphenylene sulfide powder of the production example 1 of a rechargeable lithium-ion battery, and using polyvinylidene fluoride powder (the Elf Atochem make, Kynar301F). When a part of this powder was taken out for picking and the ESR spectrum was measured, that spin concentration was increasing from below the 1017 spin / g before ozonization to 1020 spin / g. From this, it was checked that the radical has occurred in a polyvinylidene fluoride particle.

[0071] Next, 50g N-methyl pyrrolidone was made to dissolve 1g of ozonized polyvinylidene fluoride powder, and the black slurry was obtained, when it mixed until it added 60mg of graphite powder as auxiliary electric conduction material to this and the whole became homogeneous. The electrode layer containing the polyvinylidene fluoride powder which developed, dried by the same approach as in example 1, and ozonized this slurry on aluminium foil was formed.

[0072] Next, the laminating of the gel electrolyte layer used for this electrode layer in the example 1 was carried out, the lithium lamination copper foil equipped with lead wire by the same approach as in example 1 was inserted with superposition and the sheet made from polytetrafluoroethylene, the pressure was applied, and the rechargeable lithium-ion battery was produced.

[0073] (2) evaluation of a rechargeable lithium-ion battery -- when the cell produced as mentioned above was connected to the charge and discharge test machine, open circuit voltage is 1.6V and discharge to 1.0V was immediately performed by the constant current which is 0.01mA. Then, the charge and discharge test was performed by 0.01mA constant current, having carried out aging processing of this cell at 45 degrees C, and having used a positive electrode and lithium lamination copper foil as the negative electrode for the electrode layer containing the ozonization object of polyvinylidene fluoride subsequently. Consequently, the electrical-potential-difference flat part was accepted in the 1.8V neighborhood, and operating as a cell was checked. Furthermore, when the charge and discharge of this cell were repeated and carried out, over ten or more cycles, charge and discharge are possible and operating as a rechargeable battery was checked.

[0074]

[Effect of the Invention] As explained above, since the rechargeable battery of this invention contains the organic compound which ozonized the oxidation reduction reaction of an active material in the rechargeable battery used for a charge-and-discharge process as an active material of a positive electrode and a negative electrode, or one of electrodes, energy density can obtain easily the rechargeable battery which was greatly excellent in stability and safety.